

Spectroscopy of vibrational modes in metal nanoshells

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We study the spectrum of vibrational modes in metal nanoparticles with a dielectric core. Vibrational modes are excited by the rapid heating of the particle lattice that takes place after laser excitation, and can be monitored by means of pump-probe spectroscopy as coherent oscillations of transient optical spectra. In nanoshells, the presence of two metal surfaces results in a substantially different energy spectrum of acoustic vibrations than for solid particles. We calculated the energy spectrum as well as the damping of nanoshell vibrational modes. The oscillator strength of fundamental breathing mode is larger than that in solid nanoparticles. At the same time, in very thin nanoshells, the fundamental mode is overdamped due to instantaneous energy transfer to the surrounding medium.

I. INTRODUCTION

Acoustic vibrational modes in nanoparticles are impulsively excited by a rapid heating of the lattice that takes place after laser excitation[1, 2, 3, 4, 5, 6]. After initial period of rapid expansion, a nanoparticle undergoes radial contractions and expansions around the new equilibrium. The periodic change in nanoparticle volume translates into a modulation in time of the surface plasmon resonance (SPR) energy that dominates nanoparticle optical absorption spectrum. The spectrum of vibrational modes manifests itself via coherent oscillations of differential transmission at SPR energy measured using ultrafast pump-probe spectroscopy[7]. Since the size of laser spot is usually much larger than nanoparticle diameter, the initial expansion is homogeneous so that predominantly the fundamental ($n = 0$) breathing mode, corresponding to oscillations of nanoparticle volume as a whole, is excited. The lowest excited ($n = 1$) mode has weaker oscillator strength ($\approx 1/4$ of that for $n = 0$) and thus is more difficult to observe. When nanoparticle is embedded in a dielectric medium, the oscillations are damped due to the transfer of lattice energy to acoustic waves in surrounding dielectric. In solid and bimetallic particles, the size dependences of eigenmodes energy and decay rate are similar – both are inversely proportional to nanoparticle radius[8].

Here we study the vibrational modes of metal nanoshells. These recently manufactured metal particles with dielectric core[9] attracted much interest due to unique tunability of their optical properties. By varying the shell thickness during the manufacturing process, the SPR can be tuned in a wide energy interval [10]. Recent pump-probe measurements of vibrational modes dynamics in gold nanoshells submerged in water revealed characteristic oscillation pattern of differential transmission. However, the oscillations period and amplitude as well as their damping were significantly larger than those for solid nanoparticles. We perform detailed analysis of energy spectrum of lowest vibrational modes of a nanoshell in a dielectric medium. We find that the modes eigen-

ergies exhibit a strong dependence on nanoshell aspect ratio, $\kappa = R_1/R_2$, where R_1 and R_2 are inner and outer radii, respectively. Specifically, for thin nanoshells, the fundamental mode energy is considerably lower than for solid particles while the damping is significantly larger. At the same time, in the thin shell limit, the fundamental mode carries the *entire* oscillator strength which results in an enhanced oscillations amplitude as compared to solid particles. The analysis also reveals two regimes, where the spectrum is dominated by nanoshell geometry or by surrounding medium, with a sharp crossover governed by the interplay between aspect ratio and impedance.

II. SPECTRUM OF VIBRATIONAL MODES OF A SPHERICAL SHELL

We consider radial normal modes of a spherical nanoshell with dielectric core extending up to inner radius R_1 in a dielectric medium beyond outer radius R_2 . The acoustical properties of the system are characterized by the densities $\rho^{(i)}$ and the longitudinal and transverse sound velocities $c_{L,T}^{(i)}$, where $i = c, s, m$ stands for core, shell, and medium, respectively. The radial displacement $u(r)$ is determined from Helmholtz equation (at zero angular momentum) [11]

$$u'' + \frac{2u'}{r} + k^2 u = 0, \quad (1)$$

where $k = \omega/c_L$ is the wave-vector, with the boundary conditions that the displacement u and the radial component of stress tensor,

$$\sigma = \rho \left[c_L^2 u' + (c_L^2 - 2c_T^2) \frac{2u}{r} \right], \quad (2)$$

are continuous at the core/shell and shell/medium interfaces. In the three regions divided by shell boundaries,

the displacement has the form

$$\begin{aligned} u^{(c)} &\sim \frac{\partial}{\partial r} \frac{\sin k^{(c)} r}{r}, & u^{(s)} &\sim \frac{\partial}{\partial r} \frac{\sin(k^{(s)} r + \phi)}{r}, \\ u^{(m)} &\sim \frac{\partial}{\partial r} \frac{e^{ik^{(m)} r}}{r}, \end{aligned} \quad (3)$$

where ϕ is the phase mismatch. The corresponding eigenenergies are, in general, complex due to energy transfer to the outgoing wave in the surrounding medium. After matching $u(r)$ and $\sigma(r)$ at $r = R_1, R_2$, we obtain the following equations for eigenvalues $\xi = kR_2$

$$\begin{aligned} \frac{\xi^2 \kappa^2}{\xi \kappa \cot(\xi \kappa + \varphi) - 1} - \frac{\eta_c \xi^2 \kappa^2}{(\xi \kappa / \alpha_c) \cot(\xi \kappa / \alpha_c) - 1} + \chi_c &= 0, \\ \frac{\xi^2}{\xi \cot(\xi + \varphi) - 1} + \frac{\eta_m \xi^2}{1 + i\xi / \alpha_m} + \chi_m &= 0, \end{aligned} \quad (4)$$

where $\kappa = R_1/R_2$ is nanoshell aspect ratio, and the parameters

$$\begin{aligned} \alpha_i &= c_L^{(i)} / c_L^{(s)}, & \eta_i &= \rho^{(i)} / \rho^{(s)}, & \chi_i &= 4(\beta_s^2 - \eta_i \delta_i^2) \\ \beta_i &= c_T^{(i)} / c_L^{(i)}, & \delta_i &= c_T^{(i)} / c_L^{(s)}. \end{aligned} \quad (5)$$

characterize the metal/dielectric interfaces. In the ideal case of a nanoshell in vacuum, described by stress-free boundary conditions at both interfaces, we have $\alpha_c = \alpha_m = \eta_m = \eta_c = 0$ and $\chi_c = \chi_m = 4\beta_s^2$. For a thin nanoshell, $1 - \kappa \ll 1$, we then easily recover the known expression for the fundamental mode [12]

$$\xi_0 = 2\beta_s \sqrt{3 - 4\beta_s^2}. \quad (6)$$

The eigenvalue is, of course, purely real since no energy leaks through the interface.

In the realistic case of a nanoshell in a medium, the role of dielectric core is diminished. The laser pulse causes faster expansion of the metal shell than of dielectric core. Indeed, the heating of Au lattice is due to the cooling of electron gas that occurs during several ps, while the heating of dielectric core due to heat transfer from metal to dielectric takes place on a longer time scale[7]. Because a larger metal thermal expansion coefficient as compared to that of core dielectric, the shell expands to a greater extent than the dielectric core. As a result, in the new equilibrium, the core and the shell are, in fact, no longer in contact, so the boundary conditions at the core/shell interface should be taken as stress-free. This can be accomplished by setting $\eta_c = 0$. For a thin nanoshell, $1 - \kappa \ll 1$, Eqs. (4) can be then reduced to

$$\frac{\chi_c}{1 - \kappa} \left(\chi_m - \chi_c + \frac{\alpha_m \eta_m \xi^2}{\alpha_m - i\xi} \right) = \left(\chi_m + \frac{\alpha_m \eta_m \xi^2}{\alpha_m - i\xi} \right) \xi_0^2 - \chi_c \xi^2. \quad (7)$$

Typically, the density of the metal shell is much larger than that of the surrounding dielectric medium, i.e., the

parameter η_m is small. For $\eta_m \ll 1$, using $\chi_m - \chi_c = -4\eta_m \alpha_m^2 \beta_m^2$ and $\chi_m / \chi_c = 1 - \eta_m \beta_m^2$, we obtain

$$x^2 - 1 = \frac{\alpha_m \eta_m}{\xi_0 (1 - \kappa)} \left[\frac{4\alpha_m \beta_m^2}{\xi_0} - \frac{x^2}{\alpha_m / \xi_0 - ix} \right], \quad (8)$$

where $x = \xi / \xi_0$. Note that although both $1 - \kappa$ and η_m are small, their ratio can be arbitrary. It is now easy to see that there are two regimes governed by the parameter

$$\lambda = \frac{\alpha_m \eta_m}{\xi_0 (1 - \kappa)}. \quad (9)$$

For a very thin nanoshell, $\lambda \gg 1$, the lowest eigenvalue is given by

$$\xi \simeq 2\alpha_m \beta_m \left(\sqrt{1 - \beta_m^2} - i\beta_m \right). \quad (10)$$

In this regime, the energy and damping are completely determined by the surrounding medium and are independent of nanoshell aspect ratio. Note that if the medium transverse sound speed is zero (e. g., in water), then $\beta_m = c_T^{(m)} / c_L^{(m)} = 0$ and both the energy and damping rate vanish. In the second regime, corresponding to $\lambda \ll 1$, the spectrum can be obtained as

$$\xi \simeq \xi_0 - \frac{\lambda}{2} \left[\frac{\alpha_m + i\xi_0}{(\alpha_m / \xi_0)^2 + 1} - 4\alpha_m \beta_m^2 \right], \quad (11)$$

Here the real part, in a good approximation, is given by $\text{Re} \xi \simeq \xi_0$, and is independent of medium or aspect ratio, while the imaginary part, although small ($\text{Im} \xi \ll \text{Re} \xi$), depends on both. Putting all together, we obtain in this regime

$$\begin{aligned} \omega &\simeq \frac{c_L^{(s)}}{R_2} 2\beta_s \sqrt{3 - 4\beta_s^2} \\ \gamma &\simeq \frac{c_L^{(m)}}{d} \frac{2\eta_m \beta_s^2 (3 - 4\beta_s^2)}{\alpha_m^2 + 4\beta_s^2 (3 - 4\beta_s^2)}, \end{aligned} \quad (12)$$

where d is the shell thickness. Thus, for thin nanoshells, the damping rate is determined by the shell thickness rather than the overall size.

III. NUMERICAL RESULTS AND DISCUSSION

Here we present the results of our numerical calculations of vibrational mode spectrum for Au nanoshells in water. The following material parameters were used: longitudinal sound speed in gold $c_L^{(s)} = 3240$ m/s, transverse sound speed $c_T^{(s)} = 1200$ m/s, the density of gold $\rho^{(s)} = 19700$ kg/m³; corresponding values for water are $c_L^{(m)} = 1490$ m/s, $c_T^{(m)} = 0$, and $\rho^{(m)} = 1000$ kg/m³.

In Fig. 1 we show the energy and damping rate for fundamental ($n = 0$) breathing mode versus aspect ratio

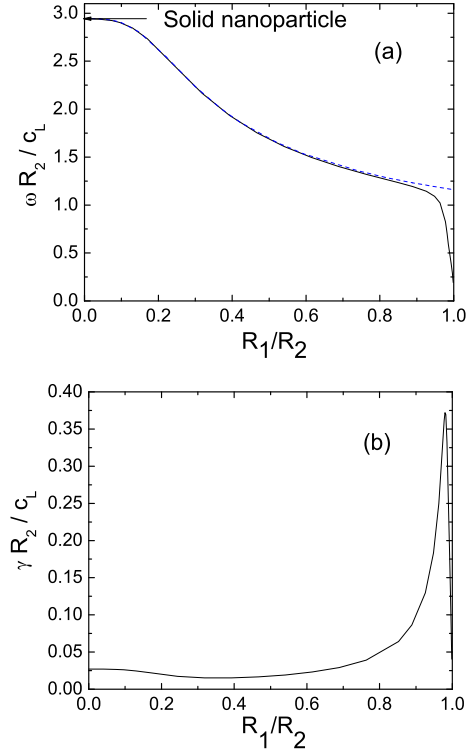


FIG. 1: Spectrum for fundamental breathing radial mode in gold nanoshell versus its aspect ratio R_1/R_2 . (a) Solid line: eigenfrequency versus R_1/R_2 in the model with free inner boundary and ideal contact between outer shell and matrix. Dashed line: eigenfrequency in the model with free boundaries. (b) Solid line: normalized damping rate versus aspect ratio.

R_1/R_2 . After the initial drop by factor of two, the frequency changes weakly for thin nanoshells in the aspect ratio range 0.6 - 0.9. In the same range, the damping rate increases by factor of four. A sharp change in behavior for very thin nanoshells with $R_1/R_2 = 0.95$ indicates the transition to overdamped regime when stored energy is instantly transferred to the surrounding medium. Note that for water ($c_T = 0$) both energy and damping rate vanish in the thin shell limit. In contrast, for $n = 1$ mode, no such transition takes place, and both energy and damping rate increase with aspect ratio, as shown in Fig. 2.

Let us now turn to oscillator strengths of fundamental and excited modes. The radial displacement $\delta r(t) = r(t) - r_0$ of a point particle inside the shell from its equilibrium position r_0 is given by a general expansion $\delta r(t) = \sum_n b_n v_n(r) e^{-i\omega_n t}$, where $v_n(r) = u_n(r) / (\int u_n^2 dV)^{1/2}$ is normalized eigenfunction of the mode with frequency ω_n . To find coefficients b_n that determine the relative contribution of n th mode, one has to specify the initial condition. We assume that the laser spot is much larger than the nanoshell overall size so that the initial rapid expansion is homogeneous, $\delta r(0) \propto r$.

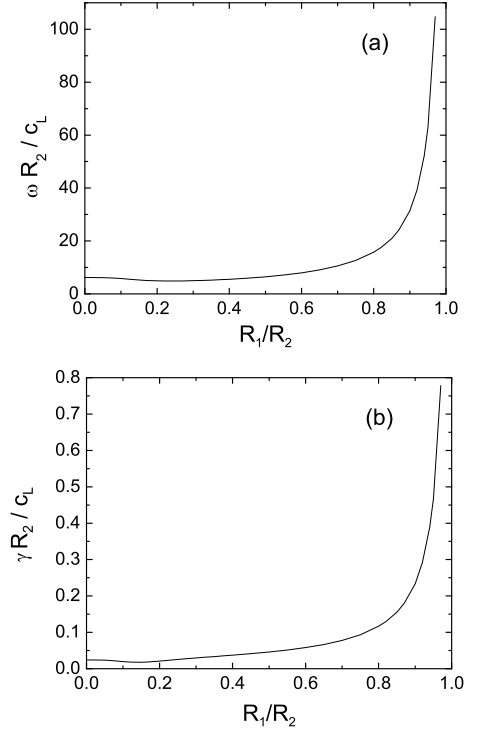


FIG. 2: Spectrum for $n = 1$ radial mode in gold nanoshell versus its aspect ratio R_1/R_2 . (a) Eigenfrequency calculated with free inner boundary and ideal contact between outer shell and medium. (b) Normalized damping rate versus aspect ratio.

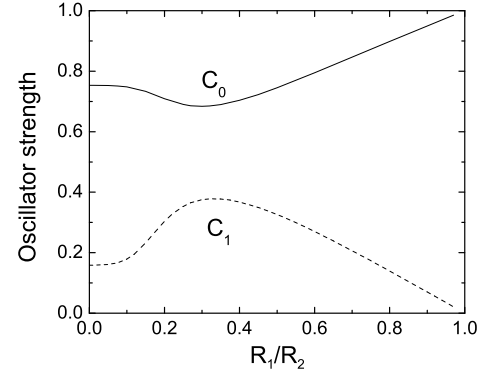


FIG. 3: Oscillator strengths for symmetric (solid line) and antisymmetric (dashed line) breathing modes of nanoshell versus nanoshell aspect ratio R_1/R_2 . At $R_1 = 0$ oscillator strength coincide with that for solid nanoparticle.

Then the expression for the n th mode oscillator strength has the form

$$C_n = \frac{b_n}{(\sum_n b_n^2)^{1/2}} = \frac{\langle r^2 \rangle^{-1/2} \int r u_n dV}{V^{1/2} [\int u_n^2 dV]^{1/2}}, \quad (13)$$

where $\langle r^2 \rangle = V^{-1} \int r^2 dV = R_2^2 \frac{3(1-\kappa^5)}{5(1-\kappa^3)}$ and V is the shell volume. In Fig. 3, we show calculated oscillator

strengths for $n = 0$ and $n = 1$ modes versus aspect ratio. In contrast to solid particles, where the relative strengths of two modes is constant, $C_1/C_0 = 1/4$, here C_1 vanishes in the $\kappa = 1$ limit. For $1 - \kappa \ll 1$, the aspect ratio dependence of C_0 can be found analytically as

$$C_0 = (1 + \kappa)/2. \quad (14)$$

In the $\kappa = 1$ limit, C_0 reaches its maximal value, $C_0 = 1$, i.e., the fundamental mode carries the entire oscillator

strength. As a result, in nanoshells, excitation of the fundamental mode should result in a greater amplitude of oscillations as compared to solid particles, while the $n = 1$ mode should be considerably weaker.

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